# Lawrence Livermore National Laboratory

# Chemical Kinetic Models for Advanced Engine Combustion

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**Lawrence Livermore National Laboratory**
**June 9, 2015**

Project ID # ACE013

DOE National Laboratory Advanced Combustion Engine R&D Merit Review and Peer Evaluation

Washington, DC

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344

LLNL-PRES-669745

# Overview

## Timeline

- Project provides fundamental research to support DOE/ industry advanced engine combustion projects
- Project directions and continuation are evaluated annually

## Budget

Project funded by DOE/VT:

- FY14: 550K
- FY15: 532K

## Barriers

- Increases in engine efficiency and decreases in engine emissions are being inhibited by an inadequate ability to accurately simulate in-cylinder combustion and emission formation processes
  - Chemical kinetic models for fuels are a critical part of engine simulation models

## Partners

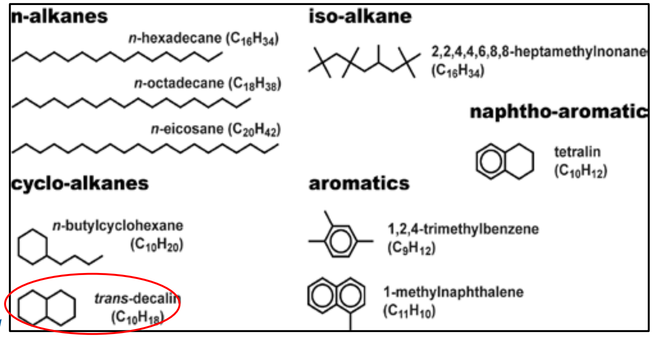
- Project Lead: LLNL – W. J. Pitz (PI)
- Part of Advanced Engine Combustion (AEC) working group:
- – 15 Industrial partners: auto, engine & energy
- – 5 National Labs & 10 Universities
- Sandia: Provides engine data for validation of detailed chemical kinetic mechanisms
- FACE Working group of the Coordinating Research Council (CRC)

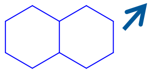
# Objectives and relevance to DOE objectives

- Objectives:
  - Develop predictive chemical kinetic models for gasoline, diesel and next generation fuels so that simulations can be used to overcome technical barriers to advanced combustion regimes in engines and needed gains in engine efficiency and reductions in pollutant emissions

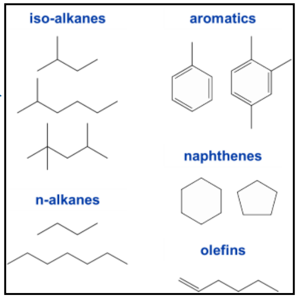
- FY15 Objectives:
  - Develop remaining kinetic model for CRC AVFL-18 nine-component diesel surrogate
  - Develop chemical kinetic models for surrogates for FACE gasoline fuels
  - Improve soot precursor models to simulate soot formation in engines

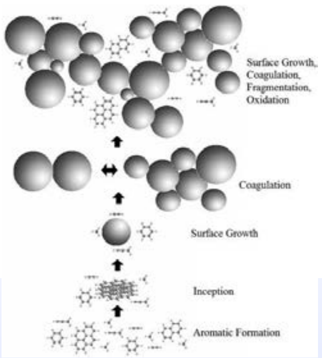
CRC AVFL-18 Diesel surrogate palette:



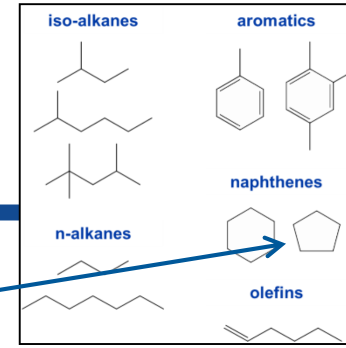



10-component gasoline surrogate palette:

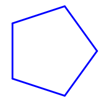


# Chemical kinetic milestones

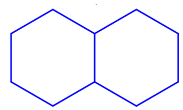



✓ Develop gasoline-surrogate component cyclopentane model (December, 2014)

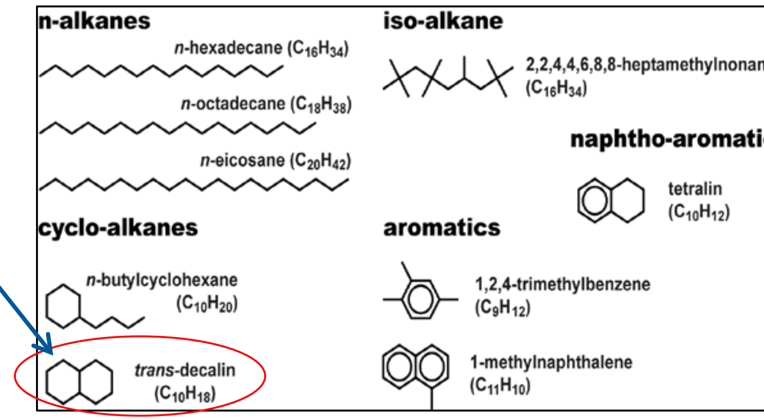


[10-component gasoline surrogate palette for FACE fuels]

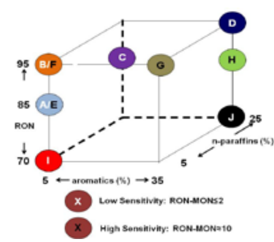
2. Develop high-temperature chemical-kinetic model for decalin (March, 2015)

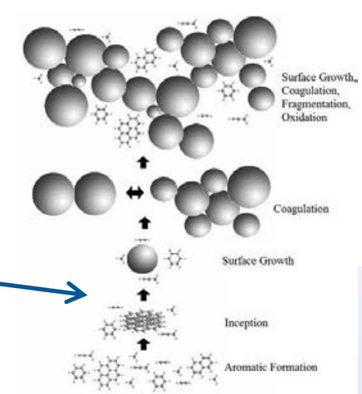


3. Develop improved chemical kinetic model for alkanes (June, 2015)(On track)
4. Develop chemical kinetic models for additional FACE gasoline fuels (Sept, 2015)(On-track)
5. Develop a preliminary semi-detailed model for incipient soot precursors (Sept, 2015) )(On-track)




[CRC AVFL-18 Diesel surrogate palette:]



# Approach

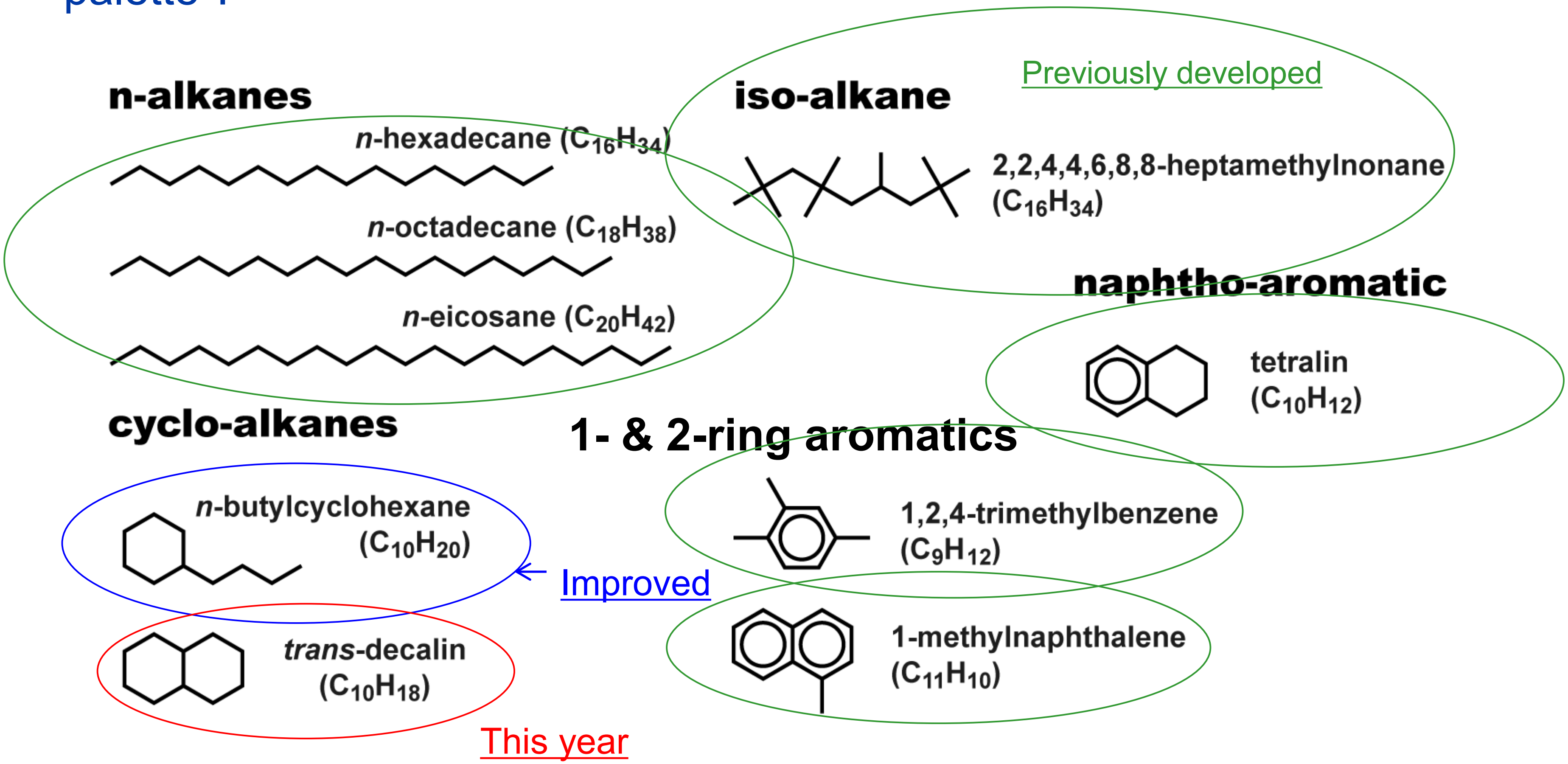
- Develop surrogate fuel models for gasoline, diesel, and next-generation fuels to enable the prediction of the effect of fuel properties on advanced engine combustion

- Develop chemical kinetic reaction models for each individual fuel component of importance for surrogate fuels for gasoline, diesel, and next generation fuels
- Combine mechanisms for representative fuel components to provide surrogate models for practical fuels
  - diesel fuel
  - gasoline (HCCI and/or DISI engines)
  - addition of ethanol and other biofuels
- Reduce mechanisms for use in CFD and multizone engine codes to improve the capability to simulate in-cylinder combustion and emission formation/destruction processes in engines
- Use the resulting models to simulate practical applications in engines, including diesel, HCCI and spark-ignition, as needed
- Iteratively improve kinetic models as needed for applications
- Make kinetic models available to industry

- Addresses barriers to increased engine efficiency and decreased emissions by allowing optimization of fuels with advanced engine combustion

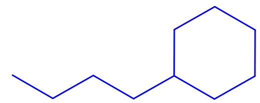
# Technical Accomplishments
# Diesel components selected for mechanism development in FY14

Components selected from the CRC AVFL-18 Diesel Surrogate palette[1]:

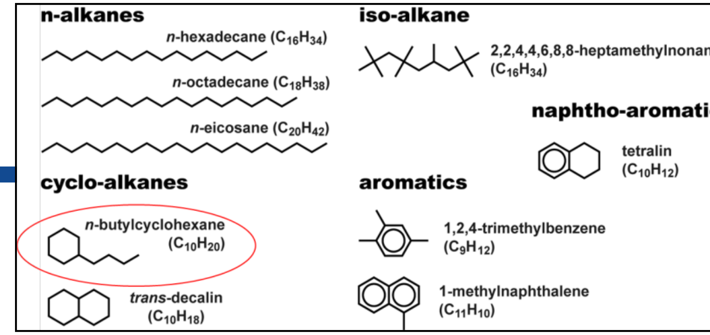



[1] Coordinating Research Council (CRC) AVFL-18 Working Group. Mueller, C. J., Cannella, W. J., Bruno, T. J., Bunting, B., Dettman, H. D., Franz, J. A., Huber, M. L., Natarajan, M., Pitz, W. J., Ratcliff, M. A. and Wright, K., Energy & Fuels 26(6):3284–3303 (2012).

# Low temperature mechanism for n-butylcyclohexane improved

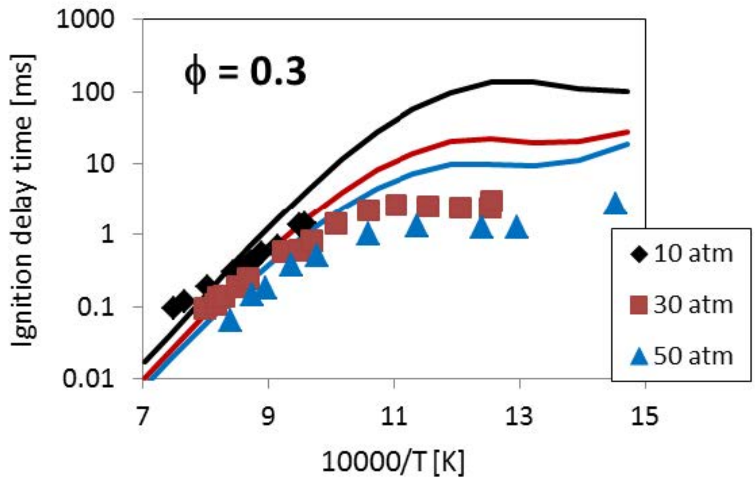


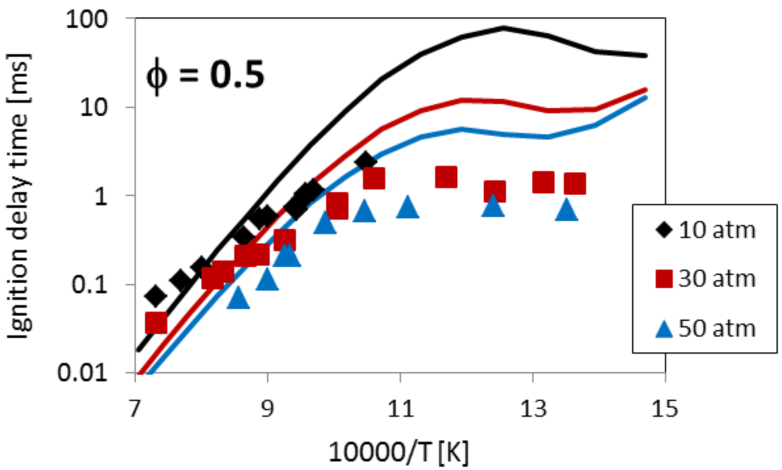
CRC AVFL-18 9-component diesel surrogate:

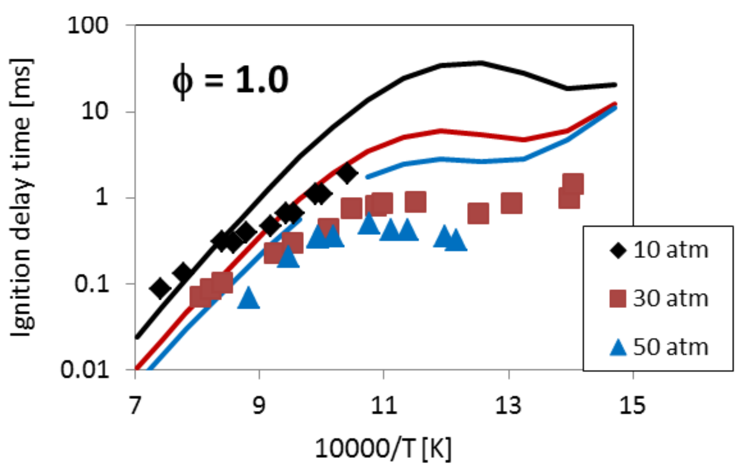


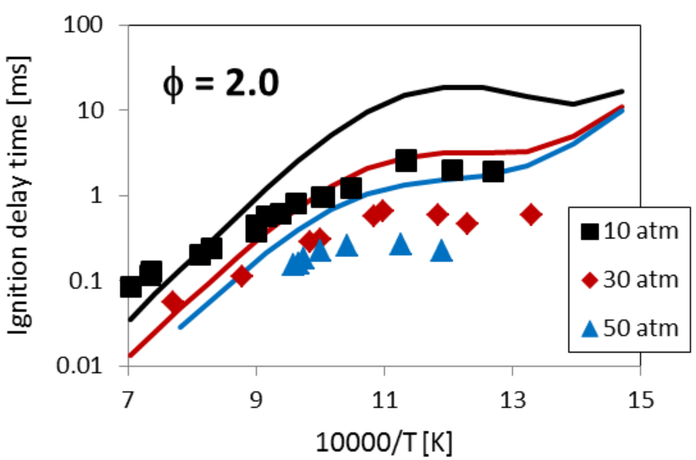

**Mechanism validated against shock-tube ignition data (Conway and Curran, NUIG, 2014):**

Previous version (FY14):

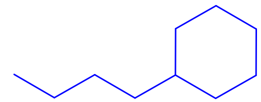


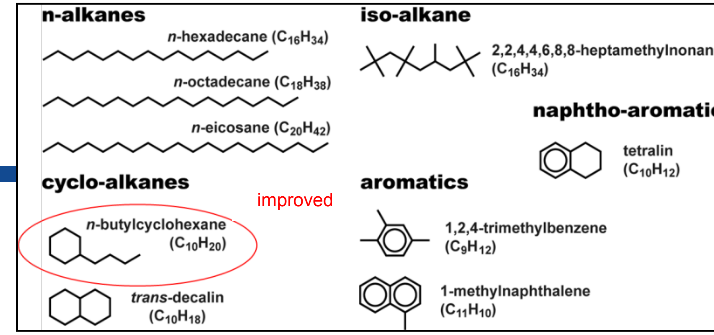



# Low temperature mechanism for n-butylcyclohexane improved

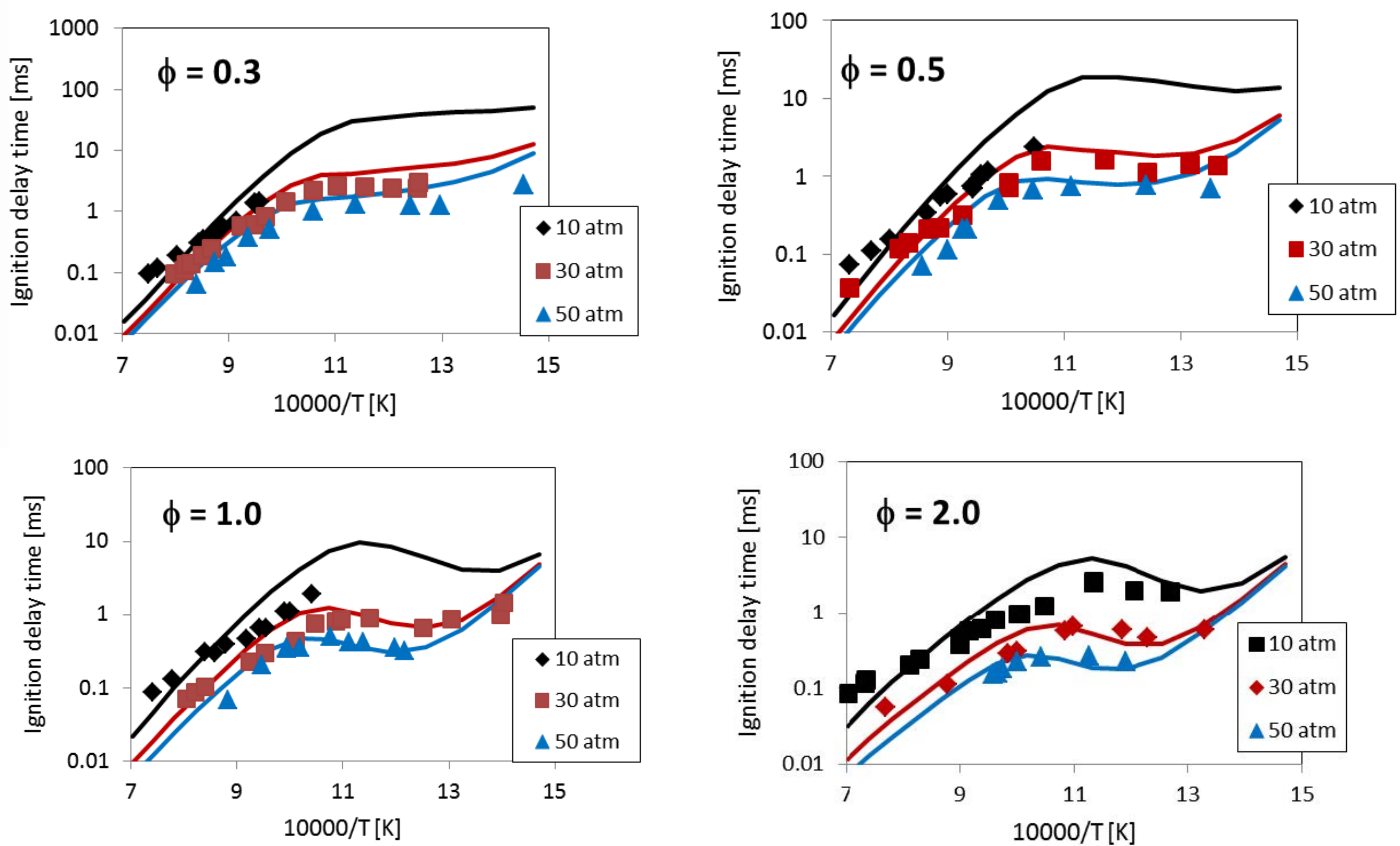


CRC AVFL-18 9-component diesel surrogate:




**Mechanism validated against shock-tube ignition data (Conway and Curran, NUIG, 2014):**

## Improved version (FY15):



# Assembled diesel surrogate mechanism for 7 of the 9 components in CRC AVFL-18 diesel surrogate palette

**4660 Species**

**18255 Reactions**

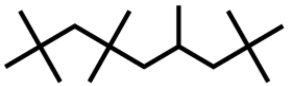
**n-alkanes**

*n*-hexadecane ($C_{16}H_{34}$)

*n*-octadecane ($C_{18}H_{38}$)

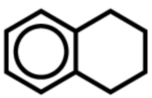
*n*-eicosane ($C_{20}H_{42}$)

**iso-alkane**



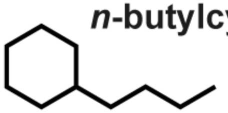
2,2,4,4,6,8,8-heptamethylnonane ($C_{16}H_{34}$)

**naphtho-aromatic**

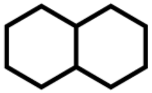


tetralin ($C_{10}H_{12}$)

**cyclo-alkanes**

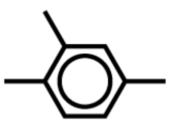


*n*-butylcyclohexane ($C_{10}H_{20}$)

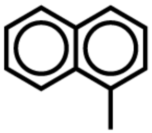


*trans*-decalin ($C_{10}H_{18}$)

**aromatics**



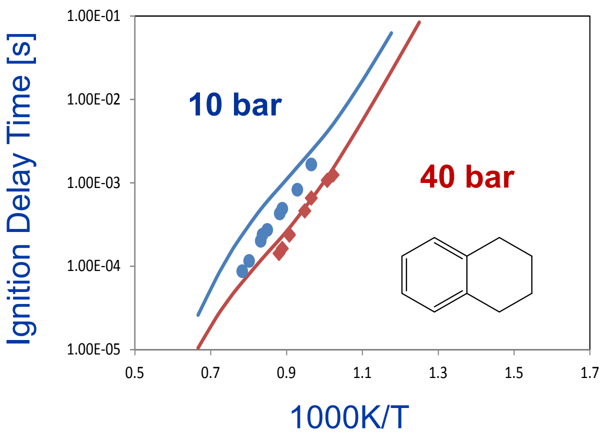
1,2,4-trimethylbenzene ($C_9H_{12}$)



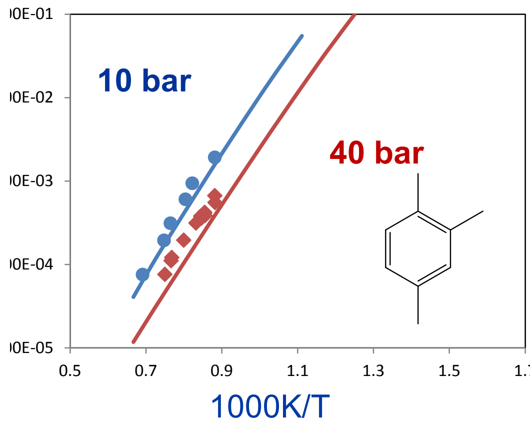
1-methylnaphthalene ($C_{11}H_{10}$)

CRC AVFL-18 Diesel Surrogate palette

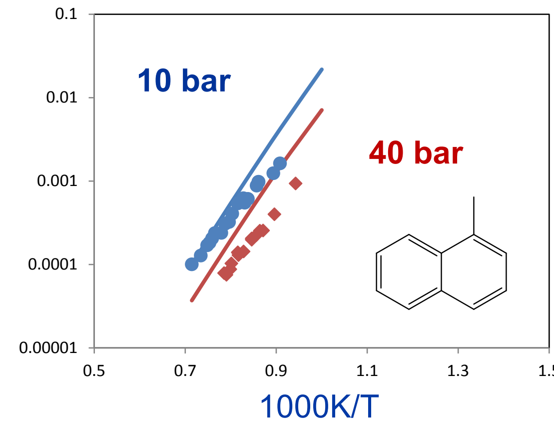
# The combined mechanism has been tested for pure components to verify that it maintains good agreement with the targets



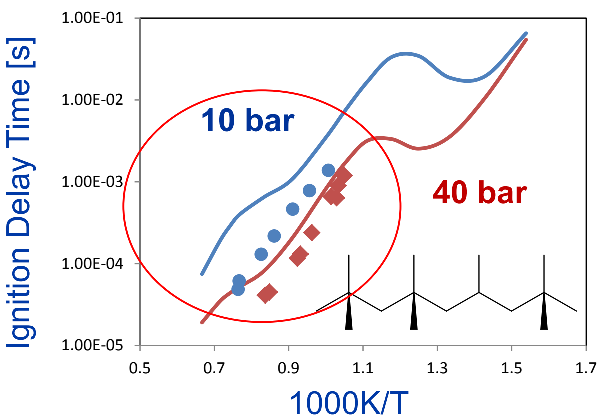

Wang et al., 2013



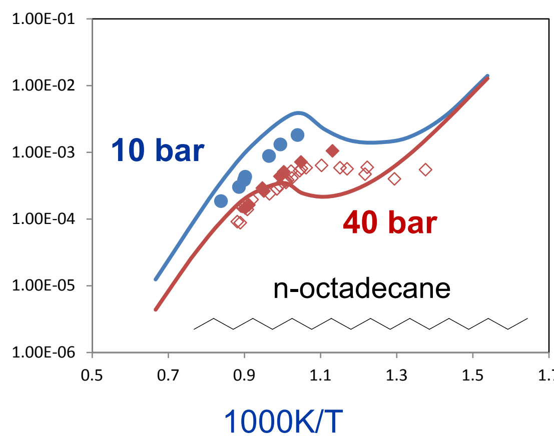

Dievart et al., 2012 (1,3,5-Trimethylbenzene)




Wang et al., 2010



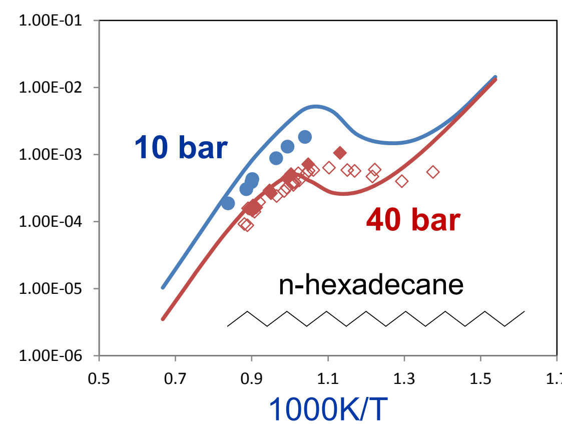

Oehlschlaeger et al., 2009




Shen et al., 2009 (for tetradecane)

Vasu et al., 2009 (dodecane)

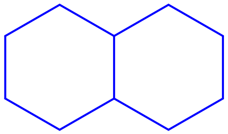
(all stoichiometric mixtures)



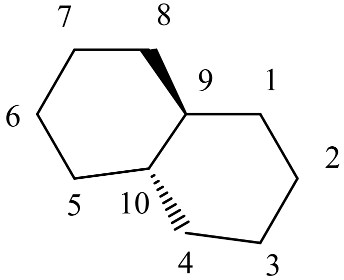

Shen et al., 2009 (for tetradecane)

Vasu et al., 2009 (dodecane)

# Decalin: High-temperature kinetic mechanism assembled



- 30 new species
- 141 new reactions
- Reaction mechanism:




```
Reaction Type 1: 1. Unimolecular fuel decomposition
!Breaks bond between C9 and C1:
!use MCH rate, multiply by 2 for degeneracy (4 C-C bonds can be broken rather than 2 in MCH)
! Assume the same fall-off as in MCH, but should be less due to more degrees of freedom in decalin
decalin = nbch-1n                       2.76E+26    -2.74       94184        ! mch = c7h14-2, Zhang,
F., et al. Energy & Fuels  27(3):1679-1687 (2013).
plog / 0.01                             1.90E+115   -28.98      140737 /     !
plog / 0.0395                           3.48E+103   -25.40      135829 /
plog / 0.197                            6.68E+87    -20.68      128511 /
plog / 0.395                            1.06E+80    -18.37      124487 /
plog / 1                                1.93E+69    -15.21      118735 /
plog / 10                               1.70E+44    -7.89       104630 /
plog / 100                              2.76E+26    -2.74       94184  /
plog / 1.0e+5                           3.80E+16     0.12       88289  /

...
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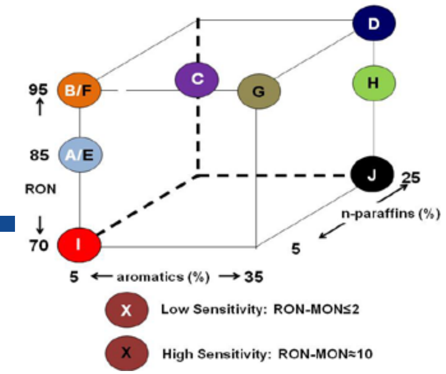
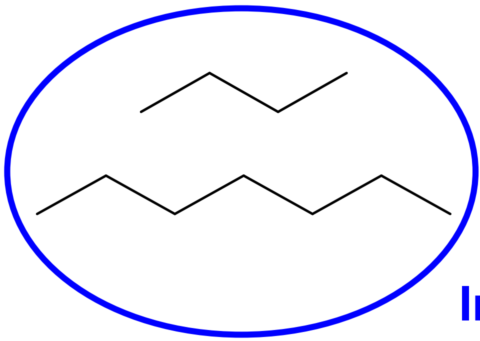
# Modeling of gasoline fuels: Developed 10-component surrogate palette to match properties of FACE gasoline fuels (FY14)

## (Collaboration with KAUST, UConn, and RPI)




**Previous work**

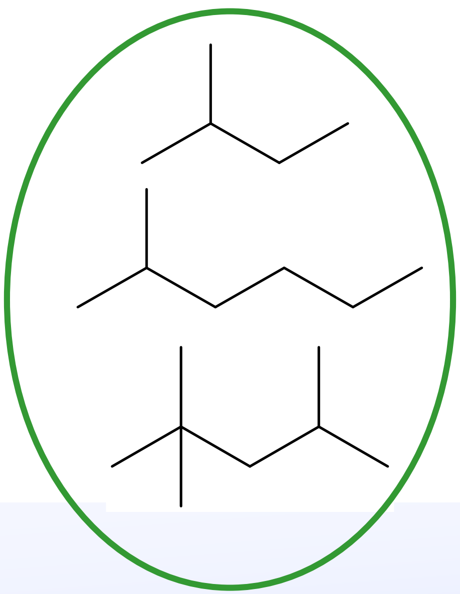
## n-alkanes:



Allow to match
the average chain length

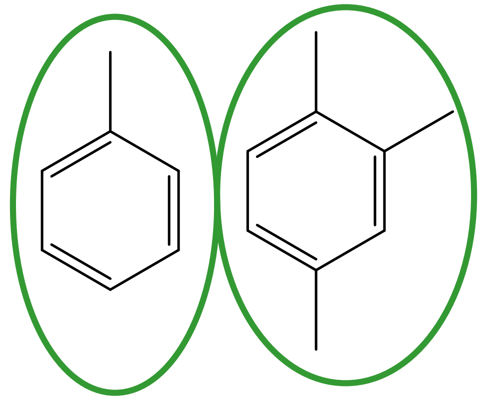
**Improved**

## iso-alkanes:



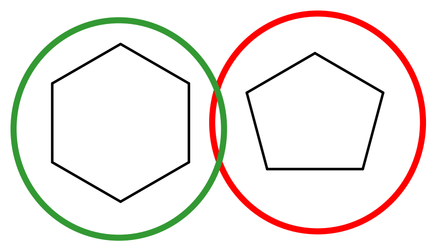
To match the average
molecular weight and the
degree of branching

## aromatics:



To match the molecular
weight and the degree
of alkyl substitution

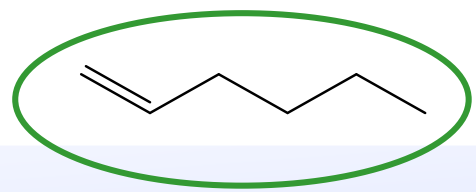
## naphthenes:



Two representative
species

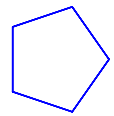
**New mechanism**

## olefins:

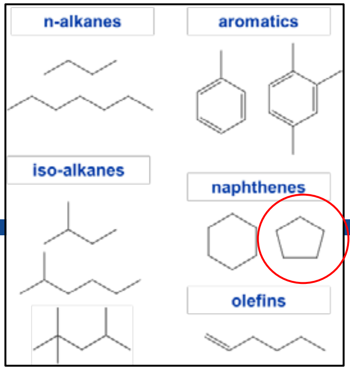


Major unsaturated
linear species

# Developed cyclopentane mechanism



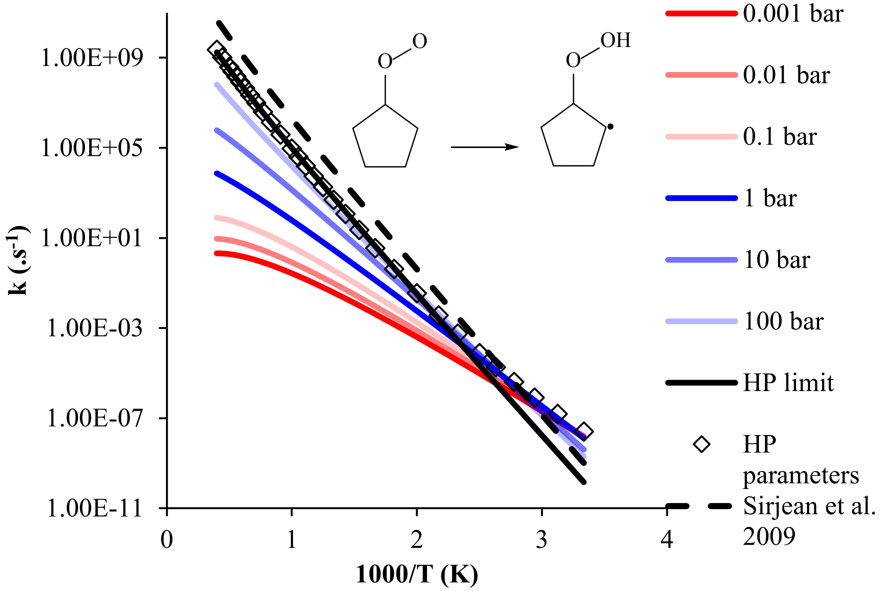
New




10-component gasoline surrogate palette to represent FACE gasoline fuels

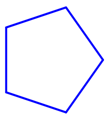
(Developed in collaboration with KAUST and NUIG)

- Mariam El Rachidi (Postdoc under Mani Sarathy from KAUST) spent 6 months at LLNL developing the mechanism:
  - Low temperature reaction rates computed in collaboration with Judit Zádor at Sandia
  - RCM ignition delay experiments by Juan Mármol, John Bugler and Henry Curran at NUIG



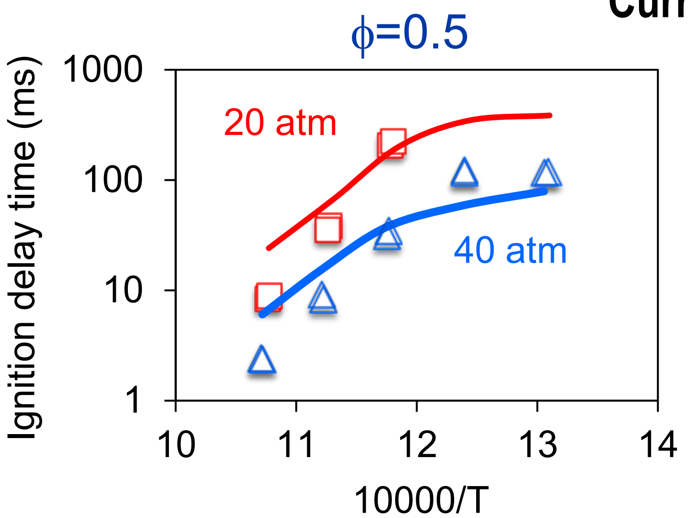

KAUST work is funded by Saudi Aramco under the FUELCOM program

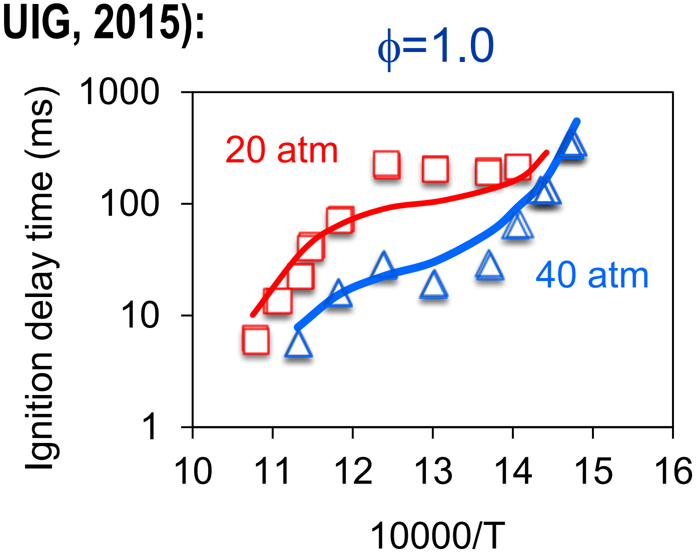
# Calculated ignition delays for cyclopentane compare reasonably well with experiments at engine-like pressures and temperatures

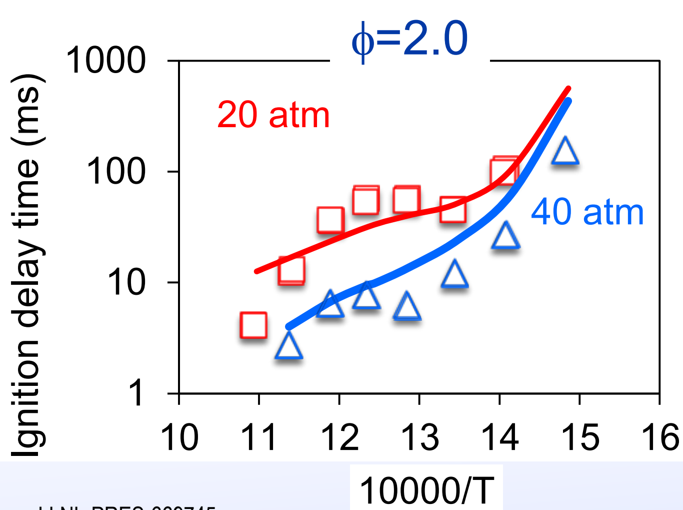


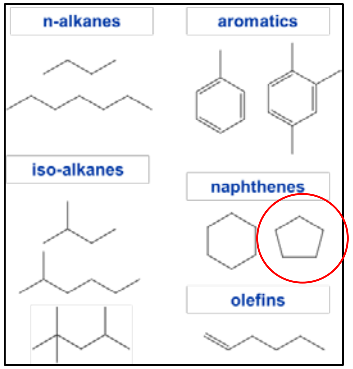
cyclopentane

**Mechanism validated against RCM ignition data (Bugler and Curran, NUIG, 2015):**



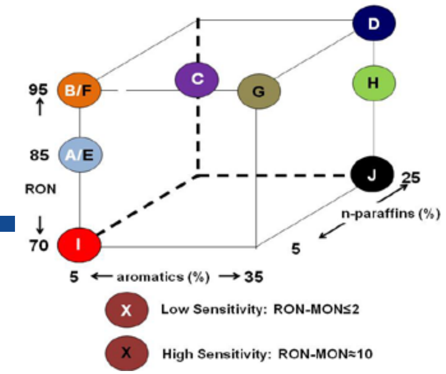



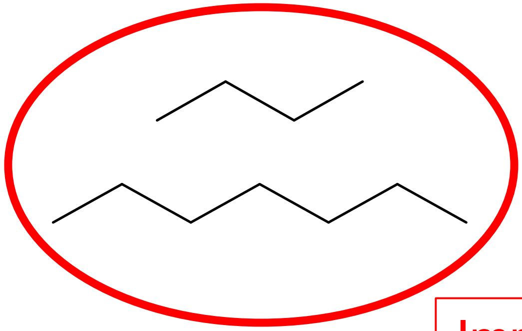




10-component gasoline surrogate palette to represent FACE gasoline fuels:

# Assembled the 10-component gasoline surrogate mechanism for FACE fuels



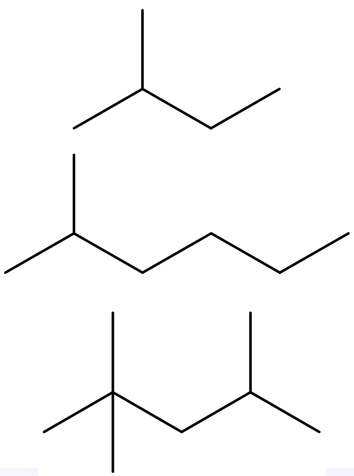

## n-alkanes



Allow to match
the average chain length

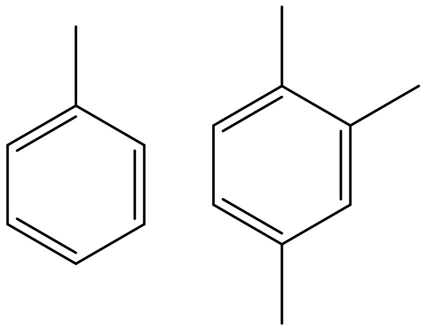
Improved

## iso-alkanes



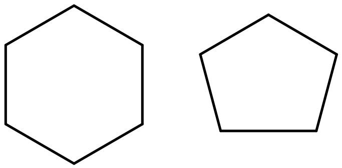
To match the average
molecular weight and the
degree of branching

## aromatics



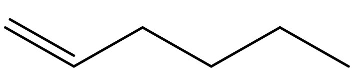
To match the molecular
weight and the degree
of alkyl substitution

## naphthenes



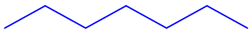
Two representative
species

## olefins



Major unsaturated
linear species

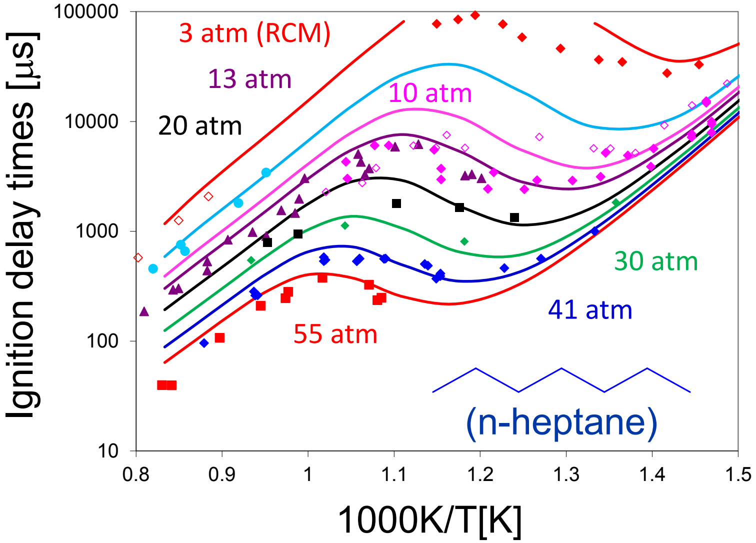
# Improved n-alkane mechanism predicts ignition at lean conditions, while maintaining good agreement at stoichiometric



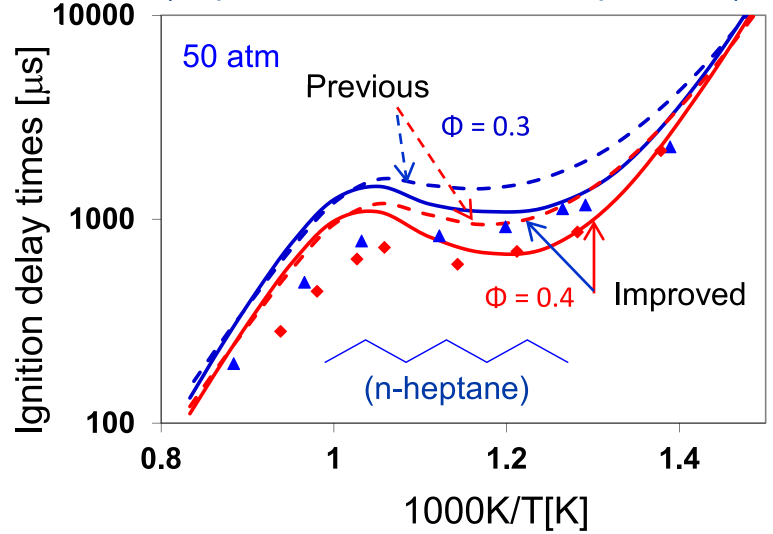
(n-heptane)

(Developed in collaboration with NUI Galway)

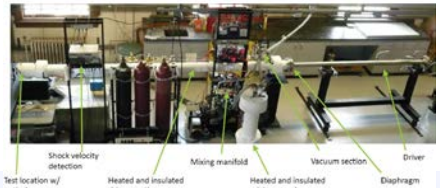
Stoichiometric:




Fuel-lean conditions:
(Important for lean HCCI operation)

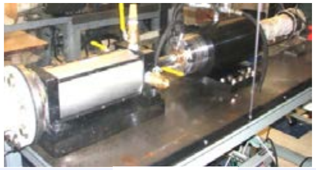



Includes an updated n-alkane mechanism based on more current fundamental rate estimates



Shock tube

Experimental data from the literature



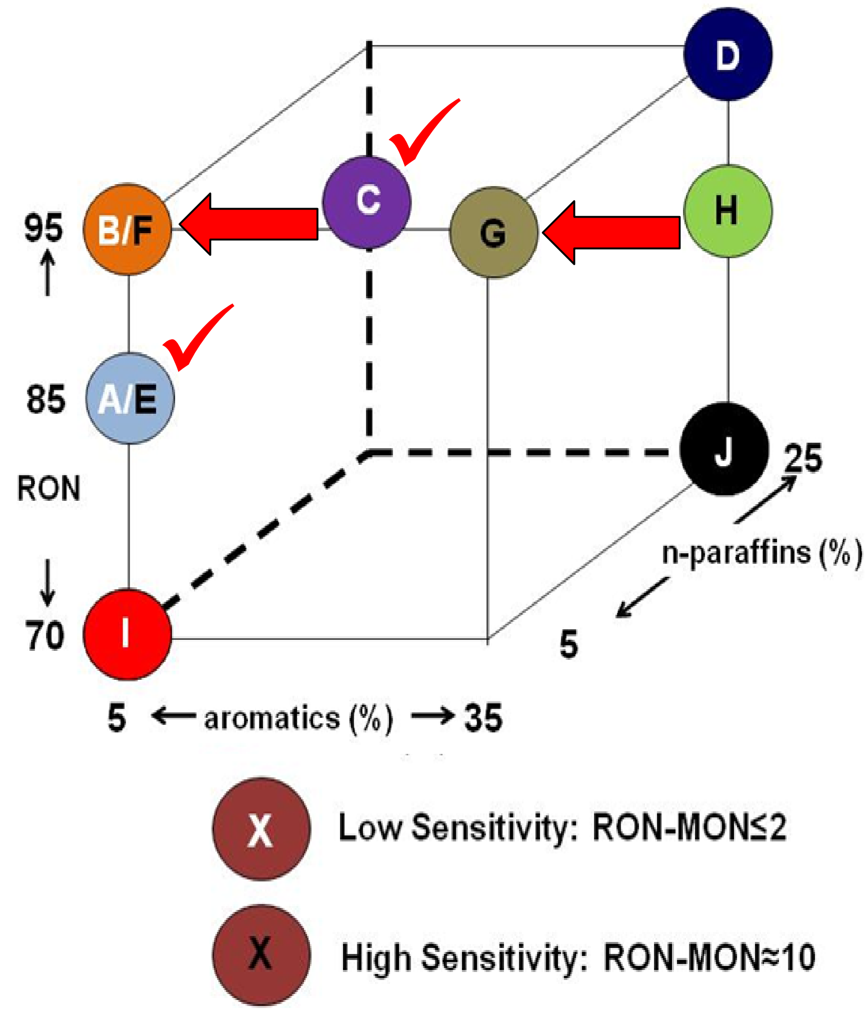
RCM

# After FACE A and C (FY14), preliminary surrogates for the FACE F and G (FY15) gasoline fuels were formulated using correlations developed by LLNL

## Comparison of Blends

| | FACE F | FACE G |
|---|---|---|
| RON | 94.4 | 96.5 |
| MON | 88.8 | 85.4 |
| AKI | 91.6 | 91 |
| Sensitivity | 5.6 | 11.1 |
| H/C ratio | 2.1 | 1.83 |
| n-paraffins* | 4.4 | 6.73 |
| iso-paraffins* | 67.56 | 38.43 |
| cycloparaffins* | 10.98 | 10.5 |
| aromatics* | 7.72 | 35.76 |
| olefins* | 9.42 | 6.82 |

*Vol %

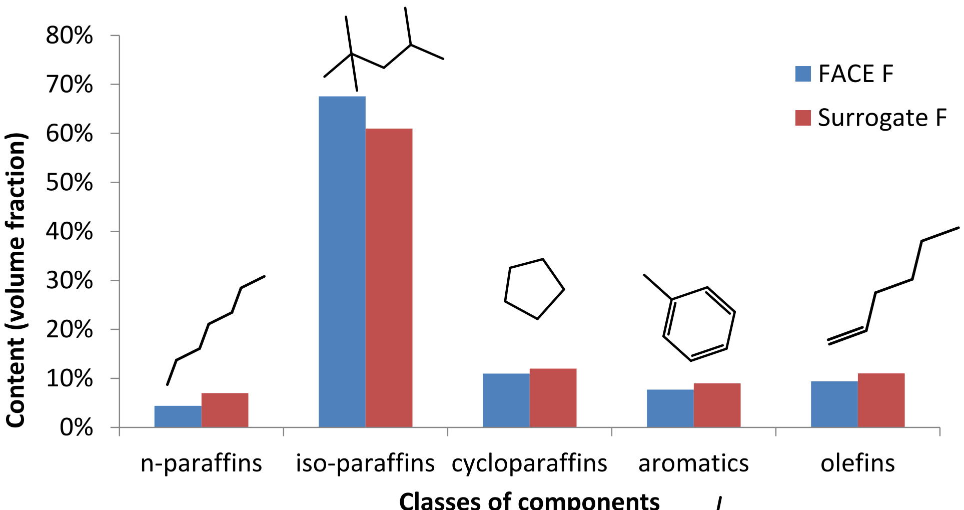



**The two gasolines have similar AKI but significantly different aromatic content. The low aromatic content of FACE F gives a lower sensitivity**

# 5- and 4- Component mixtures developed to match properties of FACE F and G gasoline fuels

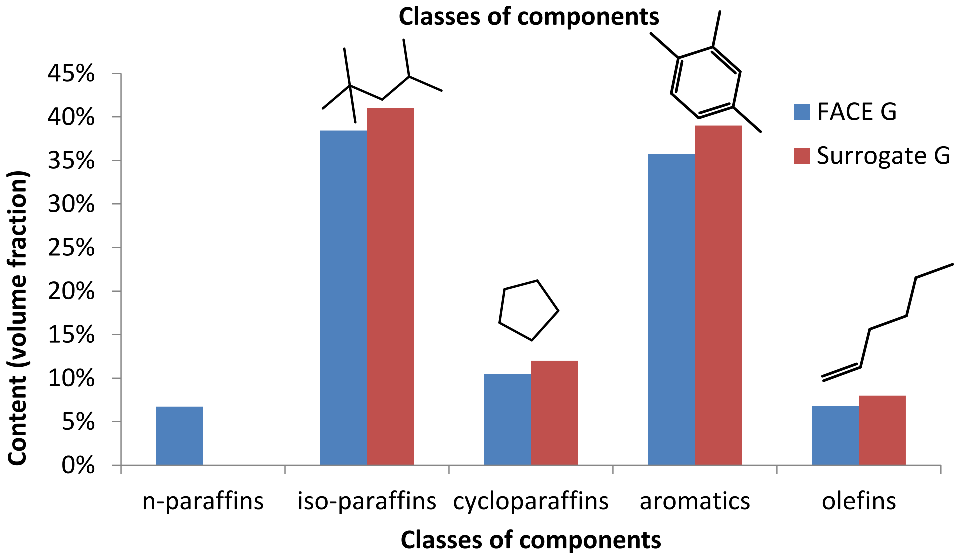
## FACE F
## 5 component surrogate

| | FACE F | Surrogate F |
|---|---|---|
| AKI | 91.60 | 91.90* |
| Sensitivity | 5.60 | 4.30* |
| H/C ratio | 2.10 | 2.07 |




## FACE G
## 4 component surrogate

| | FACE G | Surrogate G |
|---|---|---|
| AKI | 91.00 | 90.50* |
| Sensitivity | 11.10 | 10.90* |
| H/C ratio | 1.83 | 1.79 |




******Estimated using LLNL correlations***

***<u>Ongoing collaboration with KAUST, UConn and RPI targetting the validation of the model in fundamental ignition devices</u>***

# Mechanisms are available on LLNL website and by email

https://combustion.llnl.gov

## Mechanisms

### Alcohols

Ethanol
Butanol Isomers
Iso-pentanol

### Alkanes

2-Methyl and n-Alkanes
Heptane, Detailed Mechanism, Version 3.1
iso-Octane, Version 3
2,2,4,4,6,8,8-Heptamethylnonane

### Alkenes

C5 alkene

### Surrogates

**Biodiesel Surrogates**

Real Biodiesel
C10 methyl ester surrogates for biodiesel

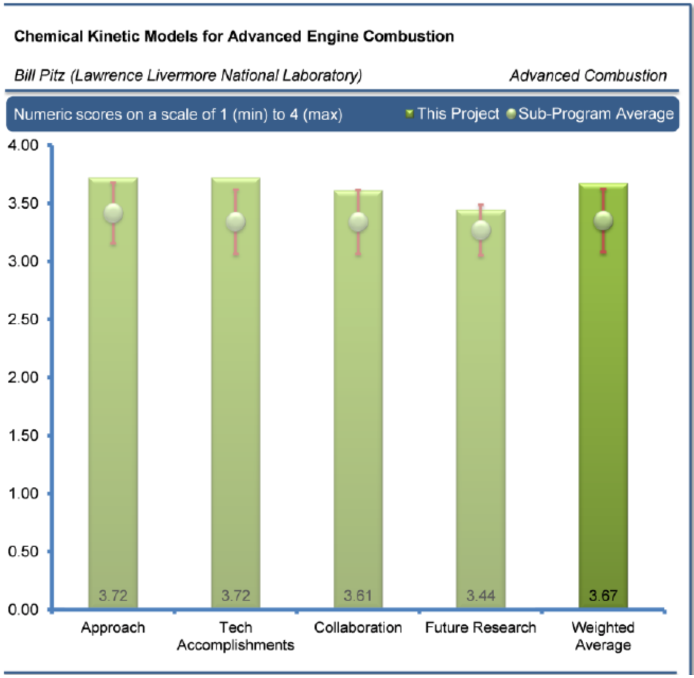
Gasoline Surrogate
Diesel PRF
Diesel surrogate, detailed and reduced

### Alkyl-Carbonates

Dimethyl Carbonate
Diethyl Carbonate
Cyclopentane

Gasoline Surrogate

# FY2014 Reviewer's comments and our response




Overall, the reviewer's comments were very positive

- The reviewer commented: This reviewer added that it would be good to see experimental validation, at the engine level, to evaluate the accuracy of the reduced mechanisms.
- Response: "The 9-component diesel surrogate mechanism will be validated at the engine level using experimental data acquired by Sandia"
- The reviewer commented: "The reviewer suggested greater coordination with industry would be useful to broaden the reach of this work"
- Response: "We have a new industry-funded project in FY15"
- The reviewer commented: "The reviewer asked at what point was more detail no longer needed for the level of simulation needed to do tasks of engineering and research, and if it was getting near to that point. The reviewer concluded that this should perhaps be addressed in the next year."
- Response: "To achieve accuracy required by engine designers, the fidelity and predictability of kinetic models need to be improved."

# Collaborations

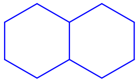
- Our major current industry collaboration is via the DOE working group on Advance Engine Combustion
  - All results presented at Advanced Engine Combustion Working group meetings (Industry, National labs, Universities)
  - Multiple exchanges of chemical kinetic models with industry
  - Collaboration on gasoline/gasoline-ethanol engine experiments with Sandia:
    - John Dec on HCCI and Magnus Sjöberg on DISI
  - Collaboration at Argonne with Sibendu Som on diesel reacting sprays and Scott Goldsborough on RCM experiments
- Second interaction is collaboration with many universities
  - Prof. Sung's group, U of Conn., Dr. Sarathy, KAUST, and Prof. Chen, UC Berkeley
  - Dr. Curran at Nat'l Univ. of Ireland on gasoline and diesel fuel components in RCM and shock tube
  - Prof. Reitz, Univ. of Wisc., on reduced kinetic models
  - Prof. Lu, U. of Conn. on mechanism reduction
  - Prof. Pfefferle, Yale, on soot chemistry
- Participation in other working groups with industrial representation
  - CRC Fuels for Advanced Combustion Engines (FACE) Working group and CRC AVFL-18a (Surrogate fuels for kinetic modeling)
- Ford: Kinetic modeling support for leaner lifted-flame combustion (LLFC)

# Remaining Challenges and Barriers

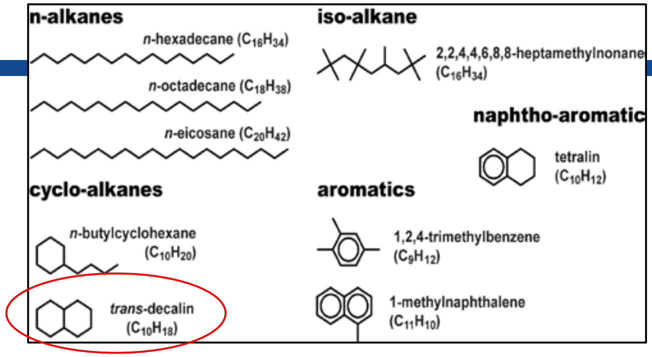
- Improve accuracy of chemical kinetic mechanisms so that desired predictability needed by engine designers can be achieved
- Develop chemical kinetic mechanisms for surrogates for diesel and gasoline fuels that are predictive at high pressures found in advanced engine combustion regimes
- Develop predictive models for  new versions of surrogates from CRC AVFL-18a that have more representative palette compounds for diesel fuels
- More accurately simulate the fuel effects with changing pressure, temperature, EGR, equivalence ratio and fuel composition

# Future plans for next year: 9-comp diesel surrogate, gasoline surrogate, ECN

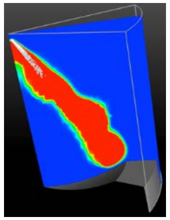
- Finish the 9-component surrogate mechanism for diesel
  - Develop low temperature mechanism for multi-ring cycloalkane



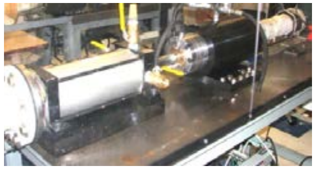
CRC AVFL-18 Diesel surrogate palette:




  - Assemble 9-component mechanism and validate
    - Provide 9-component model to LLNL fast solvers



- Validate and improve diesel surrogate model for mixtures of diesel surrogate components using RCM data from University of Connecticut

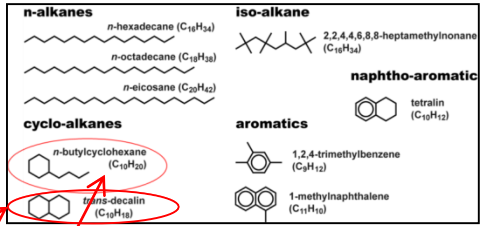


- Gasoline surrogate modeling:
  - Validate and improve gasoline surrogate model using
    - high-octane gasoline experiments in RCM at ANL
    - Gasoline surrogate (TRF + ethanol ) experiments in RCM at NUIG and RCM and shock tube at KAUST

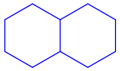
# Detailed chemical kinetic modeling summary

Developing fuel surrogate models for gasoline and diesel fuels to enable accurate advanced engine combustion simulations with fuel effects

1. Developed/refined detailed chemical kinetic models for components in 9-component CRC AVFL-18 diesel surrogate
    1. Assembled high-temperature mechanism for decalin
    2. Improved n-butylcyclohexane component model
    3. Started assembling/testing diesel surrogate mixture mechanism
2. Developed surrogate mechanisms for gasoline/gasoline-ethanol blends
    a) Developed component mechanism for cyclopentane
    b) Developed gasoline surrogate mechanisms for FACE F&G

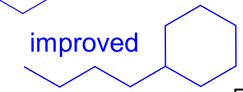



CRC AVFL-18 9-component diesel surrogate

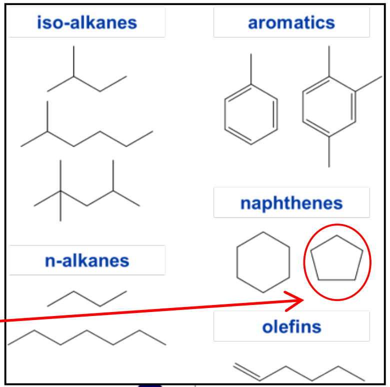


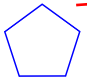
new

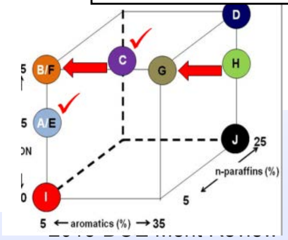
improved



10-component palette for
FACE gasoline fuels

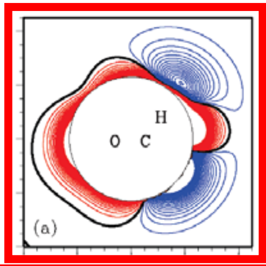




# Technical Back-Up Slides

# Chemical kinetic model development for practical fuels:



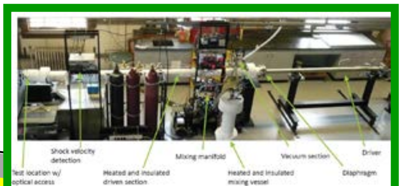

Ab initio calculations

Accurate reaction rates

Species thermodynamic properties

Reaction paths

Reaction rate rules



Twin premixed flames

Detailed Chemical Kinetic Models

Application to engines

Model Reduction

Fundamental Experiments

NUIG, UCONN, KAUST, USC, CNRS, RPI

Validation against fundamental combustion data

Fast Solvers

LLNL - Numerics

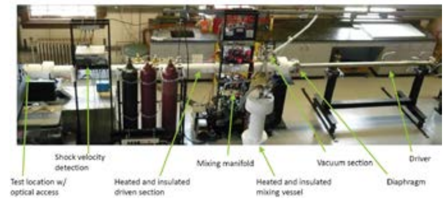
# Fuel component and surrogate models validated and improved by comparison to fundamental experimental data

Jet Stirred Reactors

Premixed Laminar Flames

Twin premixed flames

Shock tube



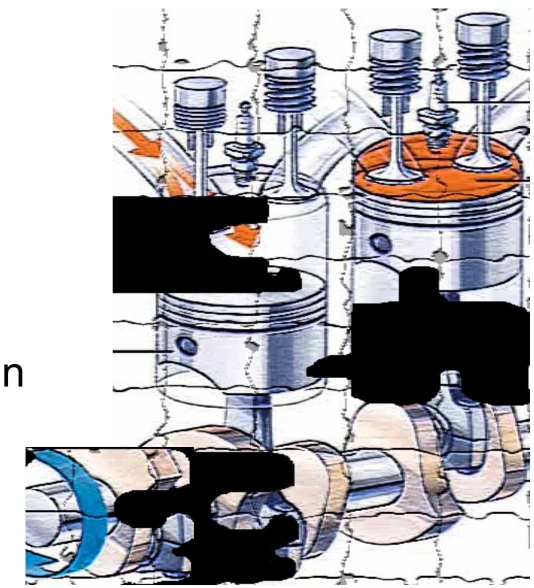

Combustion Parameters

Temperature

Pressure

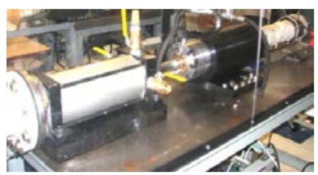
Mixture fraction (air-fuel ratio)

Mixing of fuel and air

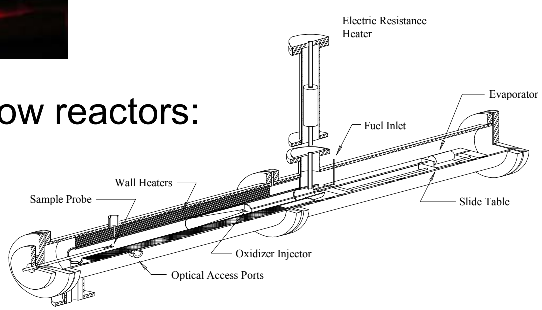


Non Premixed Flames

Rapid Compression Machine



High pressure flow reactors:

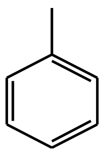
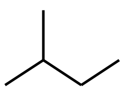
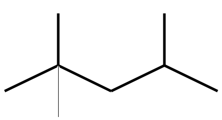
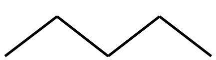
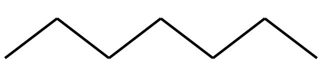



Engine Combustion

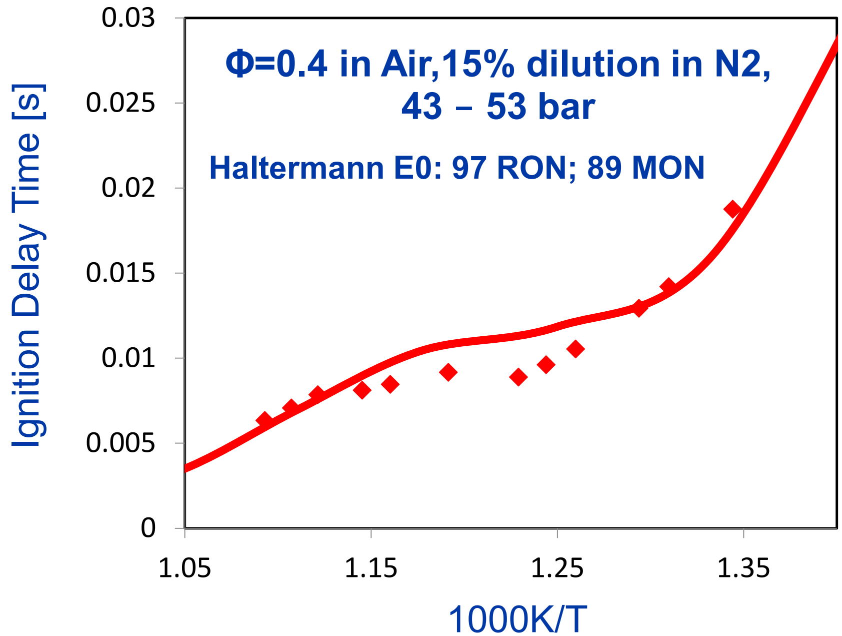
# Gasoline-surrogate model developed for high-octane certification gasoline used in recent engine experiments at Sandia

Fuel used by Dec et al. in partial fuel stratification CI experiments and Sjöberg et al. in DISI experiments

**Haltermann E0: 97 RON; 89 MON**

| 5-components | Surrogate Molar Composition |
|---|---|
|  | **37%** |
|  | **27%** |
|  | **27%** |
|  | **5%** |
|  | **4%** |

**Simulations using LLNL kinetic gasoline surrogate mechanism**




RCM experiments from Sang and Cheng at MIT

Surrogate mechanism has been recently reduced to about 250 species by Wolk and Chen at UC Berkeley